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We started the project a year ago to look for the feasibility of using alternative oxide lattice matching substrates for GaN thin film growth. In this contract, we are able to optimize the growth process to produce uncracked single crystals of LAO and LGO for substrate fabrication. We successfully grew LAO up to 50mm in diameter and LGO up to 40 mm in diameter. We have fabricated double-sided polished substrate wafters for testing.



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# FINAL Technical Report

**for the ARO Contract No: DAAH04-95-0066**

**Contract Title:** Oxide Substrates for GaN Thin Film Growth

**Period of service:** September 29, 1995 - September 28, 1996

**Principal Investigator:** Bruce H.T. Chai

**Organization:** Crystal Photonics, Inc., 2615 Westminster Terrace, Oviedo, FL 32765
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This is our last month to work on this contract and here is our final report for the entire project.

We started the project a year ago to look for the feasibility of using alternative oxide lattice matching substrates for GaN thin film growth. This is because that unlike Si, Ge, or other III-V and II-VI semiconductor compounds, there is no easy way to grow large size single crystals of GaN for substrate application. This is still true even at the end of this contract. The sapphire substrate used currently for LED production has very large lattice mismatch to the GaN film. Therefore, the search for a suitable lattice matching substrate is absolutely critical for the growth single crystal epitaxial films of GaN. We are pleased to report here that our effort this year is very successful. Not only we have demonstrated our ability to grow large single crystals LAO ($LiAlO_2$) and LGO ($LiGaO_2$) by Czochralski melt pulling technique, we also have resolved many substrate material problems to be able to grow high quality thin film of GaN with the narrowest X-ray rocking curve line width ever reported.

At beginning, we are somewhat too optimistic about the easiness of this project. It turns that our optimism is far from the reality. As the project continued, many unexpected problems started to show up. However, with all the effort putting in, we are finally able to achieve what we intend to do for the contract. Here I am listing all the critical achievements that we have made through the course of the contract:

## (I) Crystal Growth:

In this contract, we are able to optimize the growth process to produce uncracked single crystals of LAO and LGO for substrate fabrication. We successfully grew LAO up to 50 mm in diameter and LGO up to 40 mm diameter. We have fabricated double-sided polished substrate wafers for testing. When the crystal diameter is small, we have no problem to grow these crystals. However, as the diameter increases, we are facing serious problems of cracking. Between the two crystals, LAO has much less cracking problem. But the crystal has much higher scattering when shine a laser beam through the crystal. We now know the scattering problem is due to microtwining. Twining is formed during cooling and is a solid state phase transition process. Since the domain size is very small, the residue stress within the crystal is quite uniform and no crack is formed. The cracking of LGO is much worse. For a period of time we could not produce 38 mm diameter wafers, because all the crystals were cracked during cooling. After extensive studies, we now know that cracking is also due to twining. The twins were formed during growth due to many possible perturbations. We also were able to study the growth habit of LGO and find ways to produce near twin-free and crack-free LGO single crystals. As a result, we are now able to supply 38 mm diameter LAO and LGO on a steady basis. Our near term goal is to produce 50 mm diameter commercial size substrate wafers. We just recently completed the construction of two furnaces with such capacity. The actual growth will be started in October, right after the expiration of this contract. However, the work under this contract has set up a firm basis to establish the growth of crack-free LAO and LGO single crystals.

## (2) Crystal Defects and Etching Experiments:

During the development of the growth of large diameter LAO and LGO crystals, we encountered the serious problem of crystal cracking. It was not quite clear at beginning, since we examine all the crystals optically with both lasers and polarized light sources. It is a standard evaluation method to check the optical quality of all the crystals we produced. Under cross-polarized light, the crystal looks uniform in all orientations without any signs of domain structure. Since the crystal surface is normally etched by the evaporation of the charge, there are etching figures on the surface which can provide additional clue of the domains inside the crystal boule. In the case of

LAO, there is absolutely no feature on crystal surface to show any domain structure. On the other hand, for LGO, we can clearly see under oblique scattering light the boundaries between the domains. We also see similar large domains in polished LGO wafers. It is absolutely necessary to be able to grow single domain crystals. This will eliminate the crystal cracking problem and also provide domain-free substrate for GaN film growth.

Since the crystal domain can not be observed optically, we decided to use etching to reveal the domain structure. Single crystals were cut to 1 cm3 cubes for etching studies. We decided to investigate the etching in three different acids -- hydrochloric acid, sulfuric acid and phosphoric acid. We dilute the acids in four different concentrations and etch the crystal at different temperatures from 30 up to 60°C with different time intervals. We use weight loss method to estimate the etching rate and the final crystal block will have etching figures on all surfaces to provide us a three dimensional view of the domain boundaries. Regarding to the etching rate, we found that hydrochloric acid is the most efficient etchant, followed by phosphoric acid and lastly sulfuric acid. The crystal cube indeed provides us clear pictures of the domain structure. After examining the domains, it is clear that they are twining boundaries. We were quite surprised that the LAO crystal is heavily twined. The domain size in this case can be quite small down to the micron size. This is the reason why we do not see any cracking since the stress is neutralized among the small domains. On the other hand, it is also clear that the domain formation is due to post growth solid state phase transition during cooling. Since it is a fundamental thermodynamic phenomenon, there is little chance to eliminate it. However, it is still possible to grow GaN thin film on its surface, but the x-ray rock curve line width will be wider One the other hand, etching of LGO crystals reveal that the domain size is very large. It is very close to be a growth feature rather than solid-state phase transition feature. Based on the etched surface, we are able to harvest single domain materials as seed for subsequent crystal growth. The result is quite encouraging. We can now grow single crystals of LGO almost without cracking and twin boundaries. The etching experiment has help us to resolve the material problem of LGO crystals.

(3) Growth of GaN Thin Films and Crystal Reactivity:

We have fabricated standard 350 μm thick double-side polished wafers of both LAO and LGO from the crystals that we have grown. They were distributed to different places to grow GaN epitaxial thin films. The first work was done by ECR-MBE method at 850°C. The result is quite encouraging. However, there is great difficulty to grow the film by OMVPE method because the substrate reacts with the transported gas and the surface is destroyed. This is a quite discouraging result, since all the commercial film growth uses OMVPE method. We find out that both crystal surface reacts with hydrogen gas at elevated temperatures. By changing the carrier gas from hydrogen to nitrogen, it is possible to grow high quality thin film. However, the maximum temperature of deposition is still limited to below 900°C. We are now proposing to use two step growth process by first grow a layer of GaN at 850°C to form a protective layer. We subsequently raise the temperature to 1000°C to grow the GaN film at high speed. We believe that this two step growth will resolve the chemical stability problem.

One very important feature in the growth of GaN on LAO and LGO is that because the lattice constants are nearly matched, there is no need to grow a buffer layer. The GaN film can grow epitaxially directly on LAO and LGO surfaces. Also because the substrate is "softer" than the film, it will yield to compensate any stress build up due to the mismatch of thermal expansion. As a result, we have not observed any cracking of the film grown on these substrates. As mentioned before, the LAO substrate is multi-domain due to solid state phase transition, the x-ray rocking curve is broad comparable to those film grown on sapphire surface. But the nature of the broadening is totally different. For LGO substrate the result is very different. Since LGO has the closest lattice match to GaN, we have observed for the first time true single crystal epitaxial film growth. The rocking curve has the narrowest line width ($\approx$ 20 arcsec) ever reported. The result is not surprising at all. Based on the film quality, we believe that LGO is the preferred substrate to grow high quality GaN films. Our effort has now concentrated entirely on the growth of twin-free LGO single crystals.

(4) Setting up In-house Growth and Fabrication Facility:

When the contract started last year, we are leasing part of the University facility to conduct crystal growth experiment. Since April 1996, we start to build a complete crystal growth facility outside the University. It is quite an undertaken. After 5 month, we have

completed the construction of three crystal growth furnaces at our new facility with all the power supply and cooling system build up. We also clear all the zoning regulations and get all the permits for operation. The new facility started the first crystal growth in the middle of this month. At the end of this contract, we have completed the growth of two LGO crystals with 40 mm in diameter. These furnaces are design for production use with the capacity to grow up to 60 mm diameter crystals. Once the furnace is fully optimized, we will use them to grow 50 mm diameter LGO crystals. Starting in October, we have terminated our lease with the University and separated the business operation completely from the University. In addition to the growth facility, we also set up crystal fabrication facility located at New Jersey. This is because my crystal polisher still holds a job there. We plan to move his operation down to Florida in late 1977. At the crystal fabrication facility, we now have all the equipment to slice and polish the substrate wafers. The facility is in full operation. Polishing LAO and LGO substrates is not an easy task because the wafer surface reacts with the polishing agents. At present time, there is no fixed recipe established yet. We are still working on it. Our surface finish is improving continuously. We are confident that we will establish the substrate polishing procedure very soon.

Conclusion:

One year contract is completed at present time. However, we feel that we have established a lot during this one year. The most important of all is that we have proved that lattice matching oxide substrate can indeed be used to grow high quality single crystal epitaxial thin film of GaN. There are a lot of work remaining. The project will continue to eventually establish commercial use of these substrates for GaN light emitting devices.